

Collisional broadening and shifting of ammonia absorption lines at 790 nm

A. Lucchesini^a and S. Gozzini

Istituto per i Processi Chimico-Fisici del Consiglio Nazionale delle Ricerche, Area della Ricerca di Pisa, Via G. Moruzzi 1, 56124 Pisa, Italy

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Abstract. By using a diode laser spectrometer based on a commercial heterostructure diode laser operating in *free-running* mode, line shape parameters of some ammonia ro-vibrational overtones at 790 nm have been measured at room temperature. These weak absorption lines have been detected by using the wavelength modulation spectroscopy technique with second-harmonic detection. The broadening and shifting coefficients have been obtained for ten absorption lines by fitting the collected second-harmonic absorption features and varying the pressure of different buffer gases.

PACS. 33.70.Jg Line and band widths, shapes, and shifts – 33.20.Ea Infrared spectra – 07.57.Ty Infrared spectrometers, auxiliary equipment, and techniques

1 Introduction

Ammonia is a very interesting and much studied polyatomic molecule for its presence in the atmospheres of outer planets, like Saturn and Jupiter, in the interstellar space, and as a pollution tracer for its presence in the terrestrial atmosphere. Measurement of line positions and linewidth parameters are therefore useful. Many experimental and theoretical studies have been carried on so far that principally investigate the fundamental vibration levels. Although the analysis of the ammonia rovibrational spectrum is sometimes difficult for the many overlapping and interacting bands, some isolated absorption lines can be still observed and studied in different atmospheric conditions in order to get their peculiar characteristics. A high resolution spectroscopic system is essential for this purpose.

Diode lasers (DLs) gained a preeminent role as sources for spectroscopy, owing to their easy setup and control and their low cost. The cheapest ones are those emitting in the visible and near infrared and their utilization as spectroscopic tools limits the choice of the samples gases to those which have their vibrational resonances in this range. Molecules like CH₄, C₂H₂, C₂H₄, HCl, HCN, HF, H₂O, NH₃, NO₂, O₂ have transitions reachable by DLs but unfortunately the absorption lines are weak and therefore noise-reduction techniques must be used. A good compromise between complexity and good performance comes from the use of the wavelength modulation (WM) technique [1] applied directly to the diode laser spectroscopic

system. This is straightforward accomplished by operating on the injection current of the semiconductor sources.

Here by using a diode laser spectrometer we present measurements of collisional broadening and shifting coefficients of some ammonia absorption lines in the 12 600–12 700 cm⁻¹ range at room temperature (RT). They belong to the overtone $4\nu_1$ (ν_1 : symmetric stretch) and to the combination overtones $2\nu_1 + 2\nu_3$ (ν_3 : asymmetric stretch) of the symmetric top molecule NH₃ [2].

2 Experimental apparatus

Absorption measurements have been performed by using the experimental apparatus shown in Figure 1 that is set expressly for the utilization of the WM technique. The source was a InGaAlAs heterostructure SHARP diode laser (DL) Mod. LT025MD that emits 40 mW cw coherent radiation at 785 nm at RT. Thanks to its V-shaped junction cladding layer based on Sharp's original technology, this type of cw laser has a single transverse and longitudinal mode. By using a 75 MHz free spectral range (f.s.r.) Fabry-Perot interferometer we measured its FWHM emission line-width to be around 30 MHz on 100 Hz detection bandwidth, that is well below the absorption line-widths we are dealing with in this work. The interferometer transmission spectra for the LT025MD DL is displayed in Figure 2. The DL injection current was driven by a stabilized low-noise current generator, which permitted also the scan of the emission wavelength by mixing to the driving current an attenuated low frequency (~ 1 Hz) sawtooth signal. The DL was temperature controlled within 0.002 °C

^a e-mail: alex@ifam.pi.cnr.it

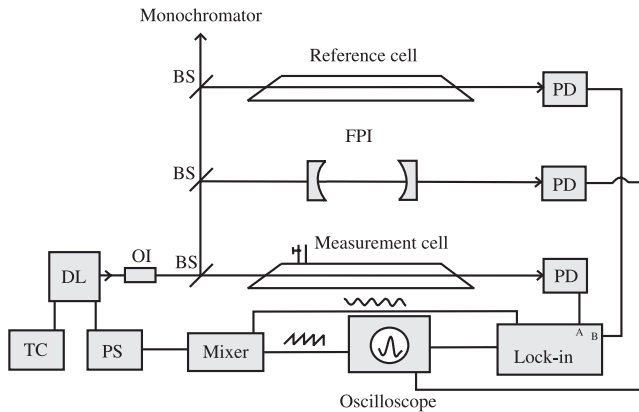


Fig. 1. Outline of the experimental apparatus. DL: diode laser; BS: beam splitter; PD: photodiode; FPI: Fabry-Perot interferometer; TC: temperature controller; PS: power supply; OI: optical insulator.

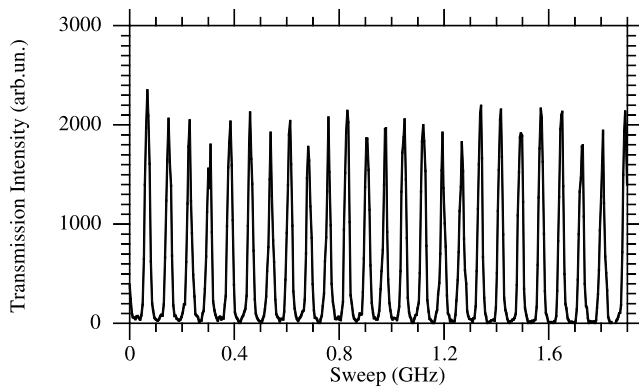


Fig. 2. SHARP LT025MD emission line shape observed through a 75 MHz f.s.r. Fabry-Perot interferometer having a finesse $F^* \sim 150$.

by a high-stability temperature controller. The temperature dependence of the diode lasers emission wavelength is critical but linear (~ 0.2 nm/ $^{\circ}$ C), and therefore one of the major requirements for using these sources is the very good temperature stabilization. The current dependence for small current variations can be considered linear too, with a slope ~ 0.01 nm/mA. In our case the DL has been used as “free-running”, that is without any external cavity configuration and feedback, therefore mode hops permit only a partial coverage of the nominal diode laser operating spectral range, but this choice is the simplest and the cheapest. The measurement cell was a 1 m long cylindrical glass cell with a 5 cm diameter, closed by two Brewster angle glass windows. The laser probe passed three times through the cell for a total of 3 m path length. A confocal 5 cm Fabry-Perot interferometer (FPI) was adopted to monitor and then linearize the scan of the diode laser over the scan range and to check the laser emission mode. A 35 cm focal length monochromator was employed for the rough wavelength reading. A reference cell equal to the measurement one, sealed at a fixed gas pressure was utilized for the line-shift measurements. All the measurements have been performed at room temperature (RT).

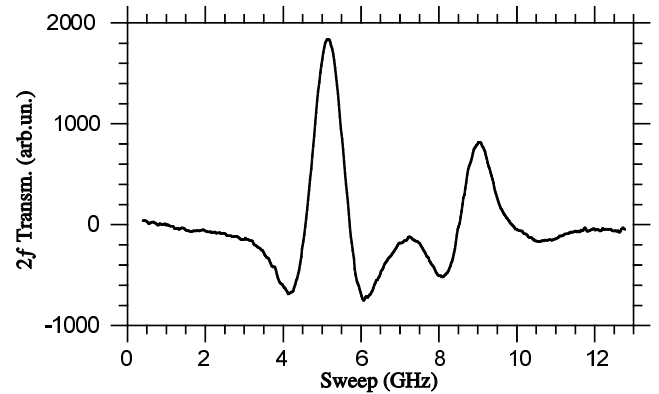


Fig. 3. 2nd derivative signal of the ammonia transmission spectrum around 787.7 nm by WM with 10 Hz bandwidth.

A sinusoidal ~ 5 kHz modulation was added to the DL injection current in order to use the phase sensitive technique. The transmission signals were collected by silicon photodiodes and sent to two lock-in amplifiers to extract the second harmonic signals. By this way, a flat and almost perfectly zero background was obtained and a good signal-to-noise ratio (S/N) has then been achieved, ranging typically from 10 to 100, depending on the gas pressure. An optical insulator was put at the exit of the DL to avoid any feedback from the several windows that could greatly increase the noise.

3 Experimental details

Ammonia has many ro-vibrational absorption lines in the 790 nm region [3], presumably belonging to the overtone $4\nu_1$ [ortho (A_1)] and to the combination overtones $2\nu_1 + 2\nu_3$ [ortho (A_1) and para (E)] [2]. More than fifty years ago spectroscopists [4] measured and tried a classification of these lines, but their spectral resolution was limited by diffraction and by the available instrumentation of that time. They used very long optical paths to overcome the problems related to the weakness of the absorptions. Now by using the diode laser radiation with a good spectral property together with the frequency modulation technique it is possible to greatly improve their results even with paths of a few meters. By taking advantage of the resolving power of a spectrometer of this kind (10^6 – 10^7), complex features can be resolved. An example of it is presented in Figure 3, where the 2nd derivative of ammonia transmission spectrum near 787.7 nm is shown; Chao [4] in 1936 could only resolve one line at 12691.50 cm^{-1} (787.712 nm at 15 $^{\circ}$ C). By using a single DL working in free-running mode it has been also possible to span more than 40 GHz without mode hops, that is more than 1 cm^{-1} . In this way the relative distances between several lines reported in literature have been checked. Many other features have been observed and some couple of lines have been found, which have also been observed by others [5] in this and other rovibrational bands of ammonia. An explanation of their existence could

be a slight asymmetry of the molecule as the amplitude of the vibration increases, allowing transitions that otherwise should be forbidden. Their precise and absolute wavelength measurement will be checked in a future work by using a wavemeter of a adequate accuracy.

3.1 Line-shape analysis

A correct line shape analysis is important when studying the pressure broadening and shifting effects on the absorption features. The right algorithm for fitting the detected features has been developed specifically for this purpose [6] and tested previously with a similar spectroscopic work on oxygen [7] in the weak absorption limit. Let us explain it in the following.

When the harmonic detection is involved, the emission frequency $\bar{\nu}$ of DLs is modulated sinusoidally by varying their injection current, giving:

$$\nu = \bar{\nu} + m \cos \Omega t, \quad (1)$$

where $\Omega = 2\pi\nu_m$, ν_m and m are respectively the frequency and the amplitude of the modulation. If $\bar{\nu}$ is slowly scanned over an interval across the chosen resonance, a signal that depends on both the line shape and the modulation parameters is observed. As an even function of the time, it can be written in a cosine Fourier series:

$$I(\bar{\nu} + m \cos \Omega t) = \sum_{n=0}^{\infty} H_n(\bar{\nu}, m) \cos n\Omega t, \quad (2)$$

where $H_n(\bar{\nu})$ is the n th harmonic component of the modulated signal. By demodulating the signal with a lock-in amplifier at a multiple $n\nu_m$ ($n = 1, 2, \dots$) of the modulation frequency, a signal proportional to the n th component $H_n(\bar{\nu})$ is collected. If the amplitude m is smaller than the width of the transition line ($m \ll \gamma$), the n th Fourier component is proportional to the n -order derivative of the original signal:

$$H_n(\bar{\nu}, m) = \frac{2^{1-n}}{n!} m^n \left. \frac{d^n I(\nu)}{d\nu^n} \right|_{\nu=\bar{\nu}}, \quad n \geq 1. \quad (3)$$

3.2 Derivative spectroscopy limits

In general the intensity of a radiation $I(\nu)$ transmitted through an absorbing medium, $I(\nu) = I_0(\nu) T(\nu)$, can be described by the Lambert-Beer equation:

$$T(\nu) = e^{-\alpha(\nu) d}, \quad (4)$$

where $T(\nu)$ is the transmittance, $d = \rho l$ is the optical density of the sample, which is the product of the gas density ρ and the optical path l of the radiation through the sample, $\alpha(\nu)$ is the absorption coefficient. In case of weak absorptions [$\alpha(\nu) d \ll 1$], that is always verified in our cases, equation (4) can be approximated by:

$$T(\nu) \simeq 1 - \alpha(\nu) d. \quad (5)$$

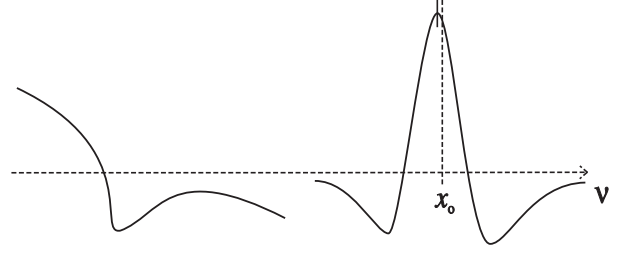


Fig. 4. Direct absorption (left) and second derivative of the absorption (right) in presence of a non constant DL emission profile (emphasized).

The absorption coefficient $\alpha(\nu)$ must take into account the contribution of the Doppler broadening and the collisional (pressure) broadening. In our measurement conditions other effects like the Dicke narrowing are not significant as it will be shown further on.

The Voigt function is the convolution of the Lorentz and the Gauss curves:

$$f(\nu) = \int_{-\infty}^{+\infty} \frac{\exp[-(t - \nu_0)^2 (I_G^2 \ln 2)]}{(t - \nu)^2 + I_L^2} dt, \quad (6)$$

where ν_0 is the gas resonance frequency, I_G and I_L are the Gaussian and Lorentzian full width at half the maximum (FWHM) respectively. Once normalized, this is the right function that describes the absorption coefficient as the radiation frequency varies.

Using the 2nd harmonic detection technique brings three important advantages: reducing the noise, increasing the resolution and zeroing the background. But when revealing on the 2nd harmonic we have to deal with the 2nd derivative of the transmitted signal. By assuming the laser emission intensity varying linearly with the frequency, *i.e.* the injection current, (for DLs this is true for frequency sweeping up to a few tens of GHz, that is a few tens of mA):

$$I_0 = \bar{I}_0 (1 + s\nu), \quad (7)$$

where \bar{I}_0 is the intensity at $\nu = 0$ and s is the fractional variation per frequency unit, the second derivative of the transmitted power will be:

$$I''(\nu) = \bar{I}_0 (1 + s\nu) T'' + 2s \bar{I}_0 T', \quad (8)$$

where $T'(\nu)$ and $T''(\nu)$ are the first and the second derivatives of the transmittance function. In the followings, in order to extract the line shape parameters, we used equation (8) through the LINEFIT 2.0 software package [8], properly modified to fit the harmonic detected signals. It adopts the Voigt approximation introduced by Martin and Puerta [9,10] through the minimum- χ^2 -method.

3.3 Line-shift analysis

Figure 4 displays the shapes of the signals corresponding to an absorption line and its second derivative in presence

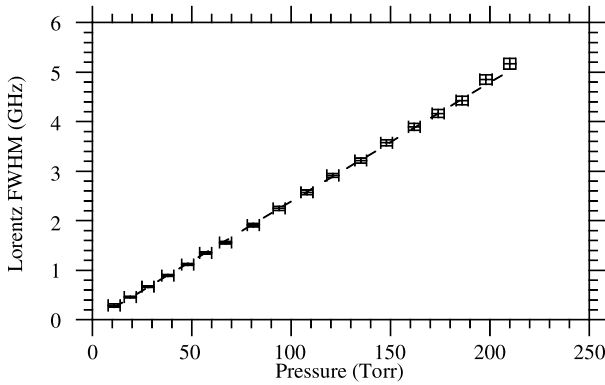


Fig. 5. Plot of the Lorentzian FWHM measurements (self-broadening) as varying the ammonia pressure for the $12\,682.719\text{ cm}^{-1}$ line at RT, along with the best linear fit.

of a linearly varying emission profile. As can be seen, the 2nd derivative signal is not symmetric and the center of the line displaces from the maximum. The apparent shift of the center depends on the slope s of the profile and on the width γ of the resonance line. This characteristic is very important when the pressure induced shift must be measured. By increasing the gas pressure, the width becomes larger and a systematic shifting of the center occurs. This is proportional to the pressure in a way very similar to the *real* pressure induced one. Thus, if the maximum of the second derivative signal is used to determine the center of the line, the measurement of the pressure induced shift will result overestimated. A much more reliable measurement of the line-shape parameters is obtained by making a fit of the second derivative signal. Nevertheless, in the fit procedure one can be induced to use simply the 2nd derivative of the absorption function, T'' , and to multiply it by a sloping linear function to match the asymmetry of the experimental signal — this is equivalent to consider only the first term on the right side of equation (8). Although at a first sight the result of the fit could seem qualitatively satisfactory, the deduced parameters are incorrect: the position of the center of the line will be again strongly affected by a *pseudo* shift. The only correct choice for the fitting function is equation (8) that implicitly takes into account the presence of a non constant background. The slope of the background can be well determined by the direct absorption signal.

Instead, in the case of the pressure broadening effect, which is ten times larger than the shifting one, the choice of only the first term of equation (8) does not induce a significative error in the fit.

4 Experimental results

Pressure broadening coefficients have been measured at RT by using the WM technique on the more intense absorption lines observed by our DL spectrometer. The Lorentz FWHM (Γ_L) component was extracted from the Voigt profile and the broadening coefficient was obtained

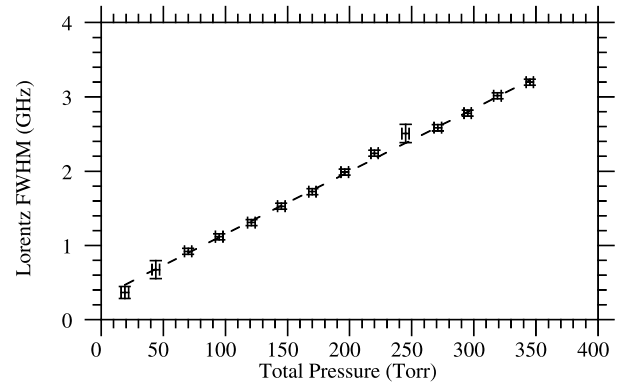


Fig. 6. Plot of the Lorentzian FWHM measurements (H_2 -broadening) as the hydrogen pressure is varied in the cell for the $12\,627.605\text{ cm}^{-1}$ line at RT, along with the best linear fit. The ammonia partial pressure was 19 torr.

by following the expression:

$$\Gamma_L(p) = \gamma_i p_i + \gamma_{\text{self}} p_o, \quad (9)$$

where γ_i is the broadening coefficient related to the buffer gas, p_i is the buffer gas pressure, γ_{self} is the ammonia self-broadening coefficient and p_o is the ammonia partial pressure.

Care has been put to control the ammonia adsorption from the measurement cells. In fact, ammonia has been reported to stick [11] to the walls of the cells and then to induce a wrong partial pressure measurement when introducing the buffer gas. This phenomenon can be identified from a non linear behavior of the FWHM when varying the host gas pressure, particularly at low pressure. To overcome this problem one can try to use cells made by alternative materials and choose the best one for the temperature at which the measurements are carried on. Otherwise an appropriate internal coating can reduce the problem to acceptable limits. In our case with glass cells at RT the effect was observable only at low He pressure when measuring the He-broadening coefficients, and was solved by ignoring the first few measurement points clearly out from the expected linear behavior with pressure. In Figure 5 there is shown a FWHM self-broadening measurement of one ammonia absorption line obtained by varying the ammonia pressure in the measurement cell at RT. The H_2 -broadening of the $12\,627.605\text{ cm}^{-1}$ absorption line is shown in Figure 6 with the best linear fit. Here the ammonia partial pressure was 19 torr and the intercept does not go to zero because of the self-broadening ($\sim 0.4\text{ GHz}$). All the errors are the maximum errors (3σ) as checked by different measurement and fitting runs. By the fit procedure and within the sensitivity of our apparatus we could not detect any collisional (Dicke) narrowing for all the observed lines. Examples of the best fit results for the $12\,682.719\text{ cm}^{-1}$ self-broadened line at three representative ammonia pressure values are shown in Figure 7 along with their respective residuals. In Figure 8 the measurement of the ammonia frequency shift by collision with He for the $12\,739.054\text{ cm}^{-1}$ line at RT is shown. The data

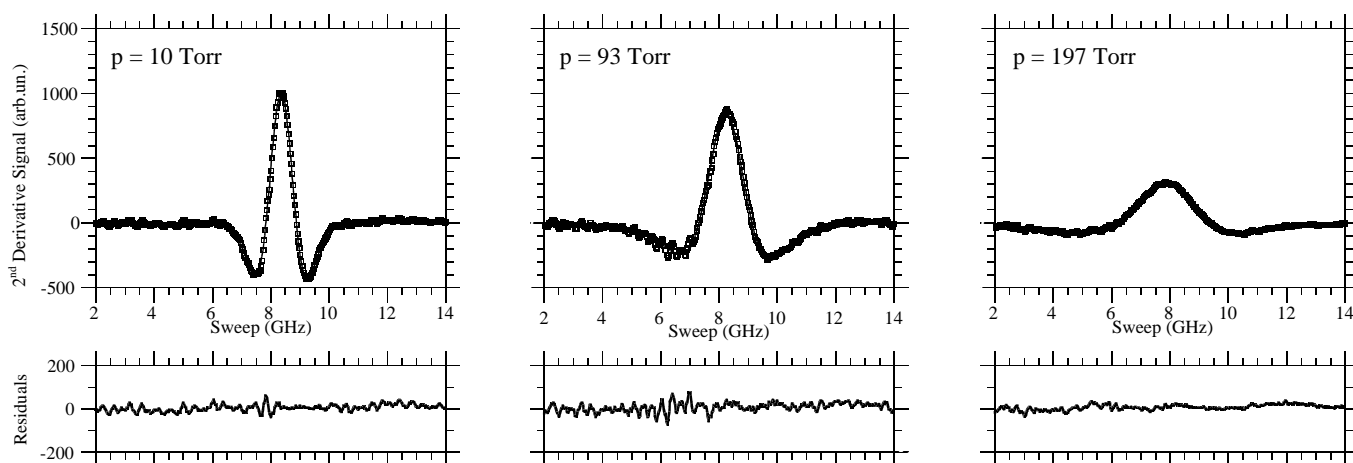


Fig. 7. 2nd derivative signals (empty squares) obtained at three significant ammonia pressures along with the best fits (solid lines) and relative residuals (same units). All the measurements are at RT and refer to the $12\,682.719\text{ cm}^{-1}$ line. The lock-in amplifier time constant was 12.5 ms.

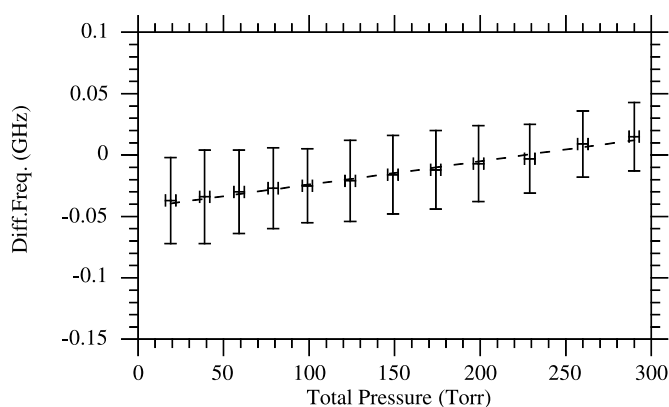


Fig. 8. Difference of the position of the ammonia $12\,739.054\text{ cm}^{-1}$ absorption line collected in the measurement and reference cells as the He gas pressure in the measurement cell is increased. The pressure is the total pressure, while the ammonia partial pressure was 19 torr. The best linear fit is shown.

do not start from zero ordinate, because there is a little phase difference between the two lock-in amplifiers used in this work. The measured absorption line broadening and shifting coefficients are listed in Tables 1 and 2 respectively, where the results related also to three buffer gases are shown. All the errors are computed for 3 standard deviations (3σ). The exact wavenumbers at RT are assigned by comparing our wavelength measurements with what observed by others by using more sophisticated Fourier transform spectrometers [12].

Because of the complexity of the absorption structure for the symmetric top molecule in this range, only partial attribution of the bands can be done. An attempt has been made by Chao [4] and among them we could observe presumably one head of series ($\nu'_0 = 12\,619.644\text{ cm}^{-1}$)

and one line ($\nu' = 12\,737.423\text{ cm}^{-1}$) of the R branch with $J = 5$. By considering the frequency interval between the lines Chao claims that they belong to one of the four parallel bands expected in this region. By taking into consideration these two lines and excluding the self-broadening, the collisional broadening coefficients decrease in absolute value as J increases as it usually happens in the fundamentals [13]. Also Coy and Lehmann [14] obtained the classification of some line in the $4\nu_1$ region by using the microwave optical double resonance (MODR) technique, but unfortunately none but the $12\,619.644\text{ cm}^{-1}$ corresponds to ours.

The big variation of the self-broadening coefficients observed from line to line in Table 1 could arise from the “collisional-coupling” effect, coming from an interference in the absorption process between adjacent spectral components, as suggested by Tarrini [15]. This specific characteristic will be the object of a future investigation.

In literature there are no measurements on this same band so far.

On the fundamentals and in particular on the ν_2 and the ν_4 , besides the work by Bouanich and coworkers [13], Baldacchini and colleagues [16,17] calculated and measured self-broadening and -shifting coefficients. Indeed their values are not far from ours, even if at very different wavelengths. Still on the ν_4 band measurements and calculations on pressure broadening of ammonia has been carried on by Dhib and coworkers [18] too.

An estimate of the spectrometer sensitivity has been performed on the strongest lines. We could still observe the lines in the measurement cell at 0.07 torr in 1 m of path. In our experimental condition this means the detection of $6.4 \times 10^{-8}\text{ g/cm}^3$ of ammonia per meter. In air at atmospheric pressure, the technique enabled to detect 50 ppm of NH_3 per meter with 1 Hz bandwidth.

Table 1. List of measured ammonia FWHM absorption lines broadening (γ) parameters at RT.

Wavenumber (cm ⁻¹)	γ_{self} (MHz/torr)	γ_{air} (MHz/torr)	γ_{H_2} (MHz/torr)	γ_{He} (MHz/torr)
12 619.644 ^a	28.7 ± 0.4	7.6 ± 0.2	8.8 ± 0.2	3.6 ± 0.5
12 627.605	22.8 ± 0.4	7.4 ± 0.1	8.5 ± 0.1	3.6 ± 0.2
12 632.919	45 ± 1	8.1 ± 0.2	8.9 ± 0.6	3.3 ± 0.5
12 666.263	25.2 ± 0.6	7.6 ± 0.1	7.9 ± 0.3	2.9 ± 0.2
12 682.719	24.0 ± 0.1	6.8 ± 0.3	8.6 ± 0.2	2.9 ± 0.1
12 686.888	39 ± 1	8.2 ± 0.9	9.6 ± 0.6	3.8 ± 0.3
12 699.080	39.9 ± 0.4	6.3 ± 0.3	8.1 ± 0.6	3.6 ± 0.8
12 708.499	22.8 ± 0.1	8.3 ± 0.7	8.0 ± 0.2	3.2 ± 0.2
12 737.423 ^a	46.2 ± 0.1	8.4 ± 0.3	7.7 ± 0.3	3.3 ± 0.3
12 739.054	45.4 ± 0.7	7.8 ± 0.1	9.0 ± 0.1	4 ± 1

Table 2. List of measured ammonia FWHM absorption lines shifting (S) parameters at RT.

Wavenumber (cm ⁻¹)	S_{self} (MHz/torr)	S_{air} (MHz/torr)	S_{H_2} (MHz/torr)	S_{He} (MHz/torr)
12 619.644 ^a	-4.0 ± 0.2	-1.0 ± 0.2	-0.9 ± 0.4	-0.4 ± 0.1
12 627.605	0.7 ± 0.2	-0.5 ± 0.2	-0.6 ± 0.1	0.3 ± 0.1
12 632.919	2.0 ± 0.1	-0.3 ± 0.2	-0.5 ± 0.2	0.0 ± 0.1
12 666.263	-2.9 ± 0.1	-0.1 ± 0.1	-0.4 ± 0.1	0.1 ± 0.1
12 682.719	-0.7 ± 0.2	-0.3 ± 0.2	-0.3 ± 0.2	0.4 ± 0.1
12 686.888	0.0 ± 0.5	-0.4 ± 0.3	0.5 ± 0.2	0.8 ± 0.1
12 699.080	0.6 ± 0.8	-0.3 ± 0.2	-0.3 ± 0.2	0.0 ± 0.1
12 708.499	-0.9 ± 0.1	-0.2 ± 0.2	-0.4 ± 0.3	0.2 ± 0.1
12 737.423 ^a	2.8 ± 0.1	-0.4 ± 0.1	-0.4 ± 0.1	0.1 ± 0.1
12 739.054	0.6 ± 0.6	-0.4 ± 0.1	-0.4 ± 0.1	0.2 ± 0.1

^a For a tentative quantum attribution of these lines see the text.

5 Conclusions

Collisional broadening and shifting coefficients for different perturber gases together with self-broadening and self-shifting coefficients have been measured at RT for some ammonia combination overtone absorption lines located around 12 600–12 700 cm⁻¹. A spectrometer based on In-GaAlAs diode laser has been employed for this purpose in its simplest configuration, that is “free-running”, by the aid of the wavelength modulation spectroscopy and the second harmonic detection technique. From line to line a big variation of the self-broadening coefficients has been observed that could arise from the “collisional-coupling” effect. In order to get rid of pseudo-effects that could mask the real broadening and shifting coefficients, special care has been put when analyzing the absorption features obtained by the wavelength modulation spectroscopy tech-

nique. The sensitivity of this diode laser spectroscopy is of the order of some tens of ppm per meter of optical path length when applied to the most intense ammonia absorptions. This makes it useful for the ammonia environmental control with typical time constants of some hundreds of milliseconds.

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